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A Computer Control and Acquisition System for Atomic Absorption Data

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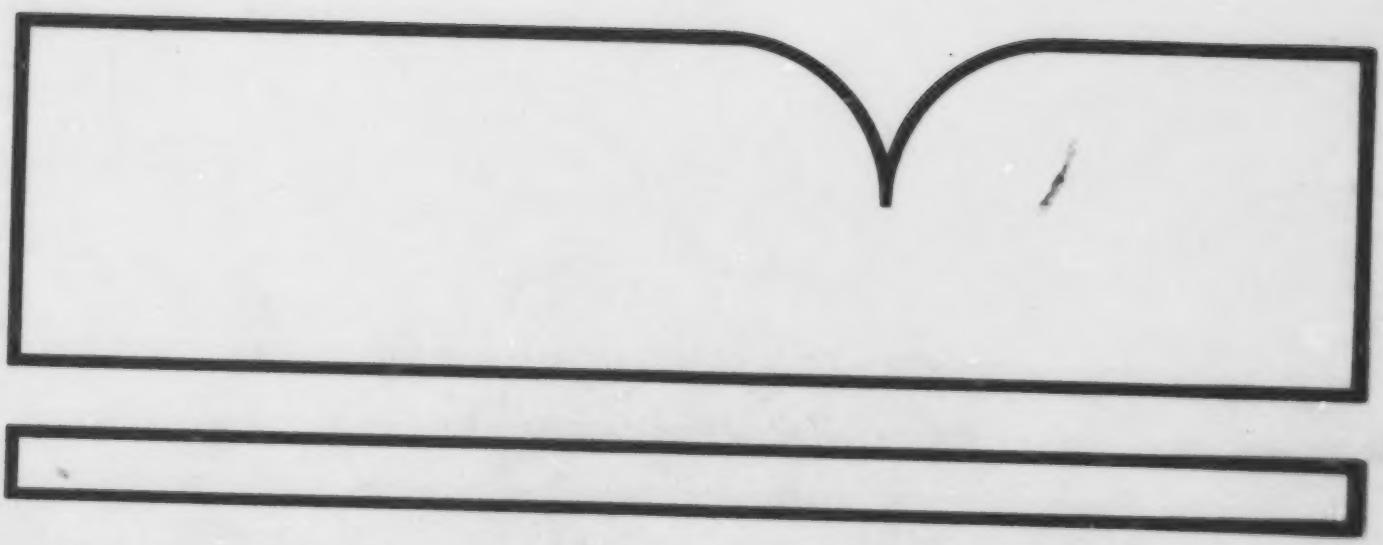

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A COMPUTER CONTROL AND ACQUISITION SYSTEM FOR ATOMIC ABSORPTION DATA

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ABSTRACT

A system is presented that controls and acquires data from a Perkin-Elmer 603 or similar atomic absorption spectrophotometer operating in the flame mode and equipped with a 200 place auto-sampler. The hardware consists of a PDP11 computer with minimum peripheral equipment and a simple instrument interface. The software is primarily a single large FORTRAN program in an RT-11, V3B operating system environment. The use of overlays reduces memory requirements to about 24 kilowords. The software provides for permanent storage of verified analytical data on a primary device and a secondary, backup device, in addition to printed reports. Data handling techniques allow correction for baseline and sensitivity drift, detection limit estimation, calculation of spike recoveries, and the use of standard additions analysis methods. Emphasis has been placed on quality control procedures, easily understood operator dialogue, and data security.

I. INTRODUCTION

Many computer-analytical instrument interface and data handling systems have been developed since general purpose computer services have become widely available. Earlier installations usually were large, multi-instrument systems because of the high cost of computer equipment and instrument interfaces.[1,5,7] When reasonably priced mini and micro computers appeared, smaller computer-instrument systems and simple interfacing schemes were designed to take advantage of the high ratio of performance to cost.[2,3,4,6,10] It is now quite common to see commercial instrumentation with a powerful mini or micro computer embedded within the system. The use of a computer separate from an internal microprocessor, as in the system described here, makes file storage of analytical data possible as well as adjustment of data to compensate for drift of instrument baseline and sensitivity. Properly done corrections of this type can improve both the precision and accuracy of the analytical data. An improvement of precision can, in turn, also improve detection limits. Measurement of these drifts is accomplished by monitoring the response of calibration blanks and standards run as unknowns during the course of an analytical session. This correction method is of particular value when analyzing complex environmental samples requiring the use of a deuterium arc background corrector.

An ideal computer-analytical instrument system would have several desirable characteristics:

1. Direct computer control of the analytical instrument.
2. Direct computer acquisition of data from the instrument.

3. A noise and crosstalk free computer-instrument interface.
4. Interactive control of computer operations by an operator.
5. Processing of instrument output to provide organized reports.
6. Adjustment of data to compensate for instrument errors.
7. Computer file storage of analytical data.
8. Storage and maintenance of quality assurance information.

All systems developed so far have at least some of these capabilities.[5,7,8,9,11,12] Operating systems in general and file management facilities in particular have been incorporated into few minicomputer controlled analytical systems because of the traditional need for large memory and disk storage resources. Memory size constraints have also limited the use of large software packages and high level languages.

In recent years, several minicomputer manufacturers have been filling this void by providing operating systems requiring minimal memory and small random access storage devices while still providing many useful services including high level programming languages. A typical example is the RT11 operating system and Fortran IV compiler offered by Digital Equipment Corporation for its PDP11 computers. Although the atomic absorption software package described here is large, nearly 40 kilowords, the overlay capability of RT11 reduces memory requirements to about 16 kilowords for the application software and 8 kilowords for the operating system, a total of 24 kilowords.

Another area which has caused difficulty in some cases is the engineering of computer-instrument interfaces. Older analytical instruments usually presented data in the form of an analog voltage which required transmission to the computer and conversion to digital form in or very near the computer. More modern instrumentation is now, in nearly all cases, capable of data output in digital format. This method of data transmission is much less susceptible to interface and transmission errors. There is, however, still a problem in ensuring that the electrically noisy environment of the laboratory does not affect the validity of the digital data. Locating the computer in a place separate from the laboratory solves part of this problem if data transmission quality can be maintained. The three chief interfacing problems that then need resolution are:

1. Elimination of interference caused by the difference in electrical ground reference levels between an analytical instrument and the associated computer.
2. Elimination of induced electrical interference in the interface electronics and connecting cables.
3. Maintenance of proper signal levels and elimination of cross-talk and reflections within the computer-instrument connecting cable.

The digital interfacing technique described here avoids all of these difficulties and, in combination with the other parts of this control and acquisition system (a PDP11 computer, the RT11 operating system, and application software), provides the services necessary to realize all of the characteristics of the ideal system listed above.

II. EQUIPMENT CONFIGURATION

Figure 1 shows the essentials of our hardware configuration. A PDP11 computer with 28 kilowords of memory is equipped

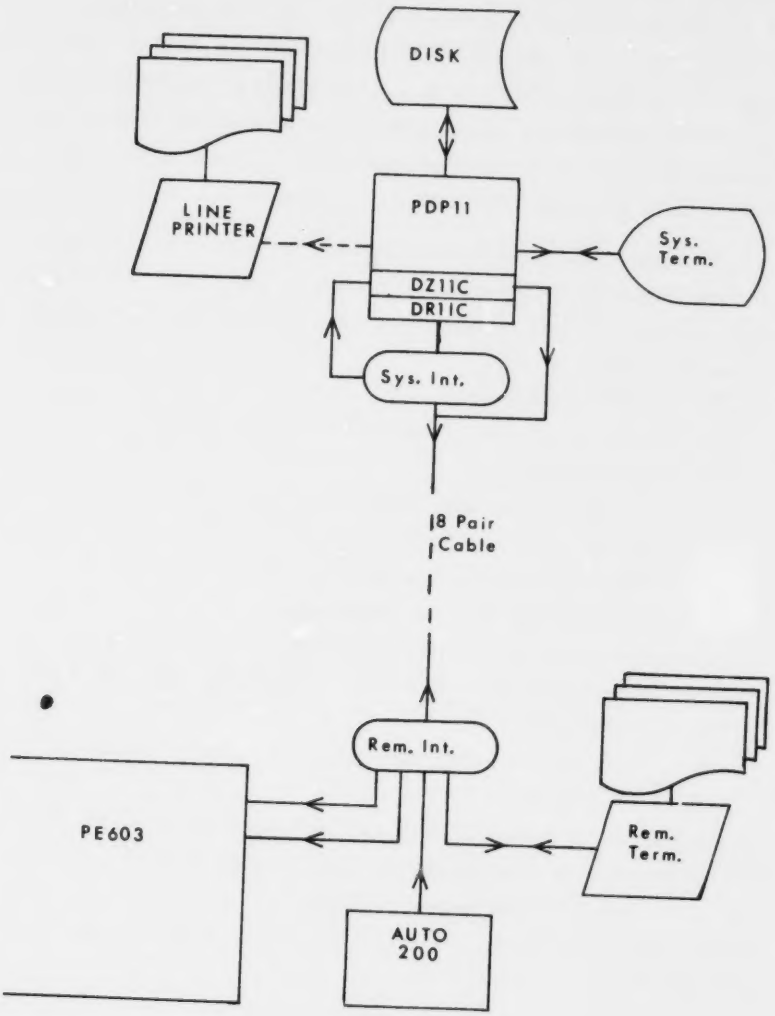


FIGURE 1.
Equipment configuration.

with a VT52 video terminal, an RK05 disk, a DATA100 line printer, a DZ11C multiple terminal control, and a DR11C general purpose interface. The DR11C and DZ11C are attached to the digital interface, which in turn is connected to a Perkin-Elmer 603 atomic absorption spectrophotometer and an LKB model 7030 sampler operated by a Perkin-Elmer AUTO-200 controller. An LA36 remote terminal completes the system.

This particular configuration does not represent the minimum necessary for successful operation of the atomic absorption data system. A typical equipment list for adequate performance is as follows:

1. A PDP11 processor.
2. Approximately 24 kilowords of memory.
3. A system terminal.
4. A random access mass storage device.
5. A DZ11C multi-terminal control.
6. A DR11C or M786 + M105 general purpose interface.
7. The described digital interface.
8. A Perkin-Elmer atomic absorption spectrophotometer (models 460, 560, 603, 703, 4000, 5000, 2280, or 2380 should work).
9. A Perkin-Elmer AUTO-200 controller and an LKB model 7030 sampler.
10. A remote terminal with 132 character width capability.

The software will also support a line printer with 132 character width and a second mass storage device if they are available. If a line printer is used, the remote terminal need have only 88 character line width.

III. INTERFACE

Figure 2 shows the construction of the digital interface used with this system. The drawing is divided vertically by a

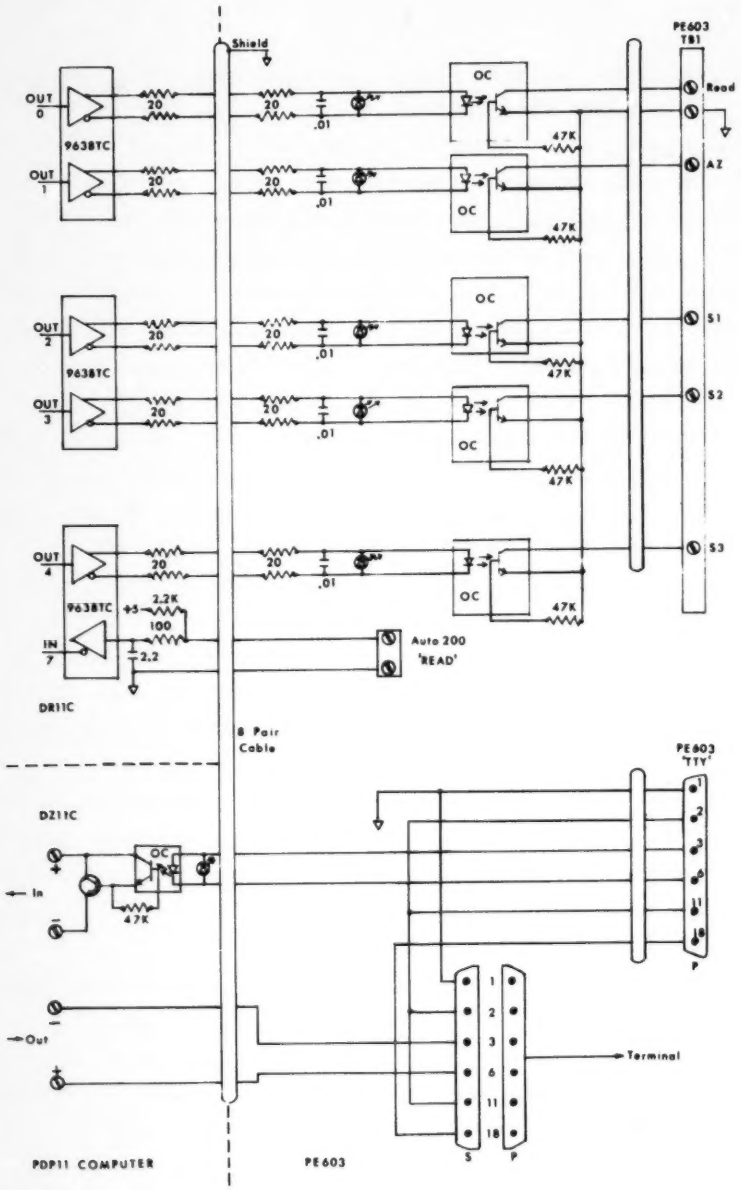


FIGURE 2.

Digital interface.

representation of an 8 twisted pair cable with overall shield which separates the interface into two parts. The left side of the figure represents the active part of the interface which is at the computer end of the connecting cable. This part of the interface requires +5 volt power. The right side represents the passive part of the interface on the instrument end of the cable. The upper left of the figure shows the connections to the DR11C or M786 interface. The lower left shows the connections to the DZ11C controller. DR11C/M786 output bits 0 through 4 are used to operate the contact closure controls available on the atomic absorption unit. The 5 output signals are conditioned with 9638TC differential line drivers matched to the twisted pair cable with 20 ohm resistors. On the receiving end, these differential signals are used to switch optical couplers (labeled OC) on or off through another pair of 20 ohm resistors. A small capacitor absorbs high frequency noise components, and a complementary light emitting diode provides a balanced load. The four 20 ohm resistors also provide the proper amount of current limiting necessary for the optical coupler and light emitting diode. The single digital input signal transmits a contact closure from the AUTO-200 to input bit 7 using the spare half of a 9638TC as an inverter. Appropriate resistors and a capacitor are used to limit current and absorb noise in this input signal.

The two other pairs in the connecting cable are used for input and output of ASCII data to and from the 20 mA DZ11C terminal control. The terminal used at the instrument location is wired to transmit keyboard data in parallel with the PE603 to the DZ11C and to receive data directly from the DZ11C. Since both the PE603 and the DZ11C generate a 20 mA current loop, a coupling device is needed. This is accomplished by the

optical coupler and transistor on the input of the DZ11C. This interface design is capable of reliable digital data transmission over large distances. Our installation uses a 100 foot cable with no problems and the length could probably be extended to more than 1000 feet if necessary.

IV. SOFTWARE

The software may be divided into 5 types, not counting the RT11 Version 3B Foreground/Background operating system:

1. The main FORTRAN program, ATOM, consisting of a root segment plus 19 overlay segments.
2. 3 auxiliary programs.
3. 8 sub-programs, including the instrument controller.
4. The remote terminal device handler.
5. 5 command files.

These software units are interrelated so that startup, operation, and shutdown of the system is very simple. For example:

1. OWNAAS, an auxiliary program used to create an empty owners file (i.e. identity of sample sources and elements analyzed for) need be executed only once when the software system is first installed.
2. One of the command files, STARTF, is executed automatically whenever the computer is powered up to set various system parameters and options. This also performs an automatic restart after power failure.
3. Another command file, ATM, makes device assignments, tests for proper configuration, executes the ATOM program, and provides analytical data storage backup if this feature is desired.

The other software modules have purposes which normally require no operator intervention:

1. Three of the command files are used only as a convenient means of compiling, linking, and producing memory maps for the ATOM program, if desired.
2. The other 2 auxiliary programs are automatically executed by the STARTF command file. One program, PRIME, sets up terminal parameters in the DZ11C controller. The other, SPOOLR, periodically searches for and prints any ATOM reports which have been directed to the line printer.
3. The remote terminal device handler, DZ, becomes part of the operating system when it is installed.

In daily use, the system operator need only turn on the computer system, enter the correct date and time, and execute the ATM command file. All interaction from this point on is via dialog with the ATOM program.

The ATOM program makes extensive use of the file management facilities in the RT11 operating system. These operations, however, are transparent to the instrument operator, who converses with the program in terms of a sample group number and an element symbol, which in turn are translated by the program into appropriate file names. The capacity of this database is 1000 groups, 80 elements, and 200 sampler positions, a total of 16 million solutions. Further extension or separation of projects is possible by means of a series identification letter, A through Z. This requires a minor program modification and results in a total capacity of 416 million solutions.

The actual limitation on storage is the size of the mass storage device. For each series, a 24 block owner's file is

required (1 block = 256 words) plus one 6 block file for each sample group. A device with 468 blocks available (e.g. DECtape or floppy disk) could accommodate (468-24)/6 = 74 sample groups which, at 200 possible sampler positions per group, is equivalent to 14,800 solution responses.

In a software/hardware system such as this, it is important to take adequate precautions against loss or corruption of computer stored analytical data. Several techniques have been used to reduce this risk to a minimum:

1. All files used are opened for imminent reading or writing and then closed as soon as the reading/writing is complete. This reduces the probability of losing a file because of computer failure to the lowest possible value.
2. All files created by the ATOM program have a definite length and contain a lock word at a strategic location within the file. Whenever a file is read, these attributes are tested. If the length is incorrect, or the lock word does not match a corresponding key word in the program, the file is regarded as corrupt. An ATOM file could become corrupt as a result of intentional tampering by a computer system operator or an unfortunate sequence of computer failures. In a normal situation, however, the probability of occurrence for either of these failure modes is very small.
3. If a second mass storage device is available, a backup copy of all ATOM files is automatically maintained. This would allow recovery even from a corrupt file situation.

Another very important concept in any sample analysis system is quality control. This system uses the following quality control procedures:

1. Every analysis group file has recorded within it the identity of the person who submitted the samples (i.e. the owner).
2. Extensive testing is done on the sequence of solutions to be aspirated to ensure that no false data can be generated by improper use of the spectrophotometer. One must, however, rely on the accuracy of the analyst in placing the solutions in proper sequence.
3. When analysis is started, the date, time, and identity of the analyst is recorded in the sample group file.
4. During analysis, all error conditions possible to detect are intercepted. If they are serious, the analysis is not allowed to continue until the error is corrected. Minor errors are flagged in the analysis record, so that the affected data cannot be used in reports or other calculations.
5. Every group of solutions must be run twice and the results of these 2 runs are compared to locate large differences caused by random instrument error. Since the probability of this type of error occurring at the same solution more than once is nearly zero, this source of error is virtually eliminated.
6. Before reports are generated, more tests of the data are made to prevent improper use of the various data correction procedures.
7. Sample reports for distribution are released only after data errors are eliminated and a responsible person verifies that the data is valid. The identity of this person, the method of sample data processing, and the

date of verification are all recorded permanently in the sample group file.

Analysis of a group of samples using the ATOM system is accomplished by operator control of the system through the use of 12 functions. Within some of the functions are several modes of operation. Some of the more important functions and their features are:

O - Originates a sample group, either by creating a new group, acquiring a previously created group, or by copying the relevant information from one element to another within the same group number. Creation of a new group requires that the operator supply a group number, an element symbol, the approximate number of sampler positions to be used, the owner's identification, and a descriptive title. Acquisition of a previous group requires a group number and element symbol. Copying requires only an element symbol.

D - Prints a directory of all sample group numbers in existence, their owners, and the elements symbols that have been specified. Either numerical order by group number or alphabetical order by owner can be selected.

I - Identifies the sample group currently ready for processing by listing all available information other than specific solution data.

S - Used by an operator to specify the contents of sampler positions. Several modes of operation allow Insertion, Deletion, Replacement, or Sequential replacement of sampler position identification with one of 12 types of solutions. The types and the information required are as follows:

-1 = Undefined: all positions of a newly created group have this initial type setting. Analysis cannot proceed until all positions are defined (i.e. set to types other than -1).

0 = Scratched: this position is processed but the results are ignored. Any type may be "scratched" at any time if the analyst decides that the solution or its response is defective.

1 = S1 (low concentration) calibration standard.

2 = S2 calibration standard.

3 = S3 (high concentration) calibration standard.

4 = AZ (auto-zero) calibration blank.

5 = Sample: requires a unique 6 character identification within the group.

6 = Calibration blank: run as an unknown.

7 = Standard: run as an unknown. Requires the concentration.

8 = Duplicate (second portion of a sample solution): requires the position of the associated sample.

9 = Replicate: treated the same way as a duplicate, but reported separately to allow evaluation of the separate but equal chemical processing that replicates receive.

10 = Spike: requires the position of the associated sample and the spiking level. Negligible dilution is assumed.

L - Prints a loading list for the auto sampler, allowing the operator to more easily ensure that the correct analytes are inserted in the proper positions.

A - Operates the spectrophotometer to accumulate analytical data. The spectrophotometer output is intercepted and reformatted to print sampler position and all other

information entered in the 'S' function along with concentration readings as the analysis proceeds.

R - Prints reports for laboratory use. A separate report corresponding to each of the unknown types listed in the 'S' function description may be selected by the operator.

M - Prints a memo of verified sample analysis data. The operator may select the samples, the elements, and their respective reporting order to appear in this report. All analyses must be within the same sample group number.

The ATOM system records the elapsed time from the start of an analysis run for every solution. This time information, along with the instrument response from blanks and standards run as unknowns, provides the means of correction for two kinds of errors encountered in most spectrophotometric techniques. One of these errors is drift of the instrument baseline with time and the other is drift of instrument sensitivity or response factor with time. Baseline drift is usually more pronounced when a deuterium arc background corrector is used. One way to counteract drift is to periodically re-zero using the calibration blank (AZ) or to recalibrate using the S1 - S3 standards. This method, however, results in a discontinuous baseline and calibration level.

The ATOM program allows the user to select either of 2 ways to handle baseline shift other than periodic re-zeroing:

1. The response of blanks run as unknowns is related to elapsed time by a linear least squares fit. The drift correction constant corresponding to the elapsed time of each solution analyzed as an unknown is then sub-

tracted from the response of that solution. This kind of baseline correction is not allowed unless certain conditions are satisfied for the solution set:

a. There must be at least 10 auto-sampler positions used.

b. No AZ calibration blank may follow any unknown.

c. At least 1/4 of the blanks run as unknowns, but not less than 1, must appear in each 1/3 of the set.

2. The responses of all blanks run as unknowns are averaged and this single correction constant is subtracted from each solution analyzed as an unknown.

Figure 3 illustrates the time-dependent correction of baseline drift. The circles represent the instrument response of blanks run as unknowns. The line is the linear least squares fit of this data as a function of elapsed time. The squares are the corrected blank responses, obtained by subtracting the value of the fit line at the time of analysis.

Sensititivity drift correction is accomplished by relating the inverse of the normalized responses of the standards run as unknowns (i.e. real concentration/instrument response) to elapsed time by a linear least squares fit. The value of the fit at the run time of each unknown is used as a multiplying correction factor for that unknown. The sensitivity correction method is not allowed unless certain conditions are satisfied:

1. Time dependent baseline drift correction must be done first.

2. No calibration standard (S1, S2, S3) may follow any unknown in the solution set.

3. At least 1/4 of the standards run as unknowns, but not less than 1, must appear in each 1/3 of the solution set.

4. The average of all standards run as unknowns must be equal to at least 1/2 of the value of the S1 (lowest concentration) calibration standard.

Figure 4 illustrates the time dependent sensitivity drift correction. The circles represent the normalized responses of the standards run as unknowns (i.e. response/real concentration). The line is the linear least squares fit of the inverse of these normalized responses, and the squares are the product of the uncorrected, normalized response and the appropriate value of the correction factor. In Figures 3 and 4, the corrected instrument response is distributed equally around the zero error position and displays a minimum amount of skewing as a function of elapsed time.

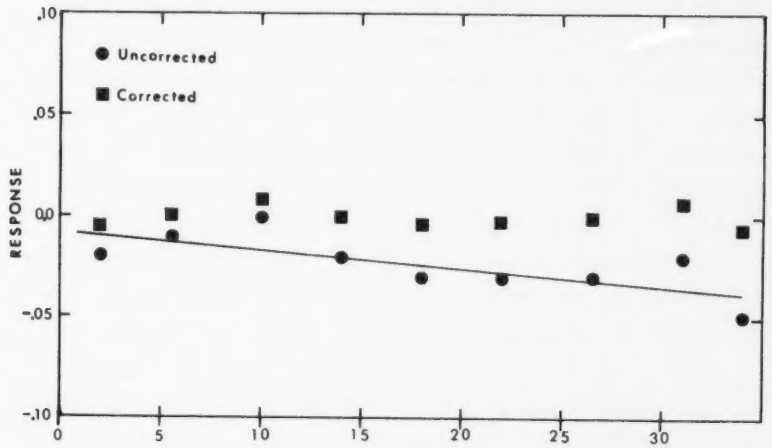
The ATOM program uses 3 standard deviations of the blanks run as unknowns as an estimate of detection limit if the following conditions are satisfied:

1. All the requirements for time dependent baseline drift correction must be fulfilled.
2. There must be at least 5 blanks run as unknowns in the solution set.

When an operator requests report generation using function 'R', and all the appropriate conditions have been met, the program prints linear least squares fit statistics tables to aid in the selection of suitable means for data correction. If more than 10% of the blanks or standards run as unknowns have caused minor errors during analysis, however, the corresponding correction procedure is not allowed. The operator may select the procedures he desires for data processing from among those allowed using either his judgement or the results of statistical tests of significance performed by the program. After this, he may select the reports he wishes. After a sample

FIGURE 3.

Baseline drift correction.



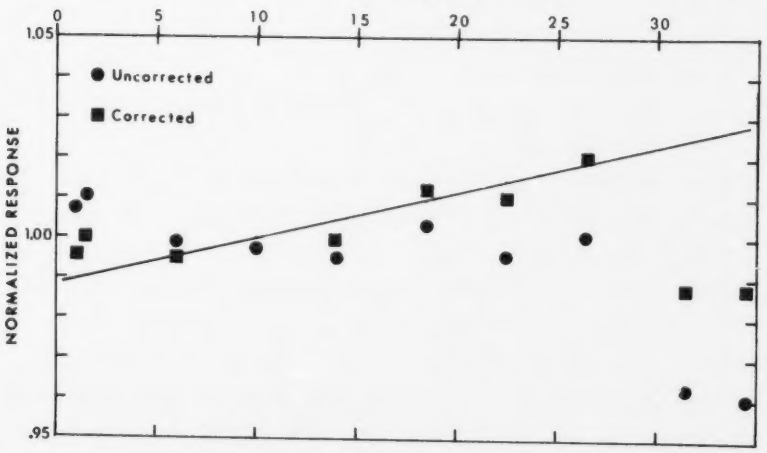


FIGURE 4.

Sensitivity drift correction.

report is printed, and if there were no errors during analysis, the operator is asked to verify the sample data. If he elects to do this, the processed sample data, the date and the verifier's identity are all saved in the sample group file and are available for preparing a memo report of analysis (function M).

V. OPERATION

A typical analysis might proceed as follows:

1. After receiving a group of samples for analysis, the analyst/operator looks at the last directory to select an unused group number and, using the 'O' function, creates a new group.
2. He then uses the 'S' function to specify the contents of all the positions needed in the auto-sampler and makes a loading list using function 'L'.
3. After making corrections to the loading list, if necessary, using function 'S', he fills the sampler tubes and loads them into the correct positions of the auto-sampler.
4. Two analysis runs are completed using function 'A' and normal auto-sampler procedure.
5. If no serious errors occur during analysis, the operator requests reports using function 'R'. He examines the correction statistics, selects an appropriate correction method and detection limit, and requests reports.
6. If there were no errors, and a sample report was generated, the operator verifies the sample data.
7. If there are other elements to be analyzed for, the analyst uses the 'O' function to copy the loading list to the next element, uses the 'S' function to make

whatever minor changes are required, and repeats the analytical cycle from step 3.

8. After all required analyses are completed and verified, the operator requests a memo report for the samples and elements desired using function 'M'.

The reports for laboratory use produced by function 'R' contain complete information about the analysis of a specified group. Space considerations do not allow reproduction of legible examples of these reports here. A sample report however, contains the values of all calibration standards used, the detection limits, the data handling method, and the date, time, and analyst identification for each run. In tabular form are the auto-sampler position, sample identification, and for each run the elapsed time, the instrument response, the amount of baseline drift subtracted, the sensitivity drift correction factor used, and the resulting adjusted response for each run. The product of the overall and individual dilution factors is also printed along with the final result, the average of both runs multiplied by the dilution factor and labeled with the proper units. Report concentration units may be set by a mode of the 'S' function.

The operator/analyst is never required to manipulate analytical data during the operation of the ATOM system and, after the initial sample specification phase, need not enter any other sample information. Data evaluations of the instrumental drift, detection limit estimates, standards performance, duplicate sample agreement, spike recoveries, etc. are all provided by the system as soon as the analysis is complete. Because of the computer file storage of analytical instrument responses and other information, all printed reports and the loading list can be reproduced or recalculated using the same or a different data handling method at any time.

VI. SUMMARY

The more important aspects of a software and interface system for controlling and gathering data from a Perkin-Elmer 603 or similar model spectrophotometer using the ubiquitous PDP11 computer is described. The system is designed to provide many of the characteristics of a large computer-instrument system but requires only minimal equipment. By fairly simple modification, a user could adapt this system for use with a graphite furnace equipped spectrophotometer. It is also possible to modify the software to accomplish non-linear drift correction if the quality of the data warrants it and a user so desires. There are many other aspects of this system that make it easy to learn and interact with which have not been discussed here. A more complete installation and user's manual, detailed plans for the interface, and the software are all available from the author at no cost.

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